

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : C22C 14/00, C23C 8/10	A1	(11) International Publication Number: <b>WO 96/23908</b> (43) International Publication Date: <u>8-August 1996 (08.08.96)</u>
--	----	---

(21) International Application Number: PCT/US96/01123

(22) International Filing Date: 23 January 1996 (23.01.96)

(30) Priority Data:  
08/381,719 31 January 1995 (31.01.95) US

(71) Applicant: SMITH & NEPHEW RICHARDS INC. [US/US];  
1450 Brooks Road, Memphis, TN 38116 (US).

(72) Inventors: MISHRA, Ajit, K.; 6915 Stone Ridge Drive #127,  
Memphis, TN 38115 (US). POGGIE, Robert, A.; 303 Betty  
Lane, Mine Hill, NJ 07803 (US). DAVIDSON, James, A.;  
2573 Windy Oaks Drive, Germantown, TN 38139 (US).

(74) Agents: KRIEGER, Paul, E. et al.; Pravel, Hewitt, Kimball &  
Krieger, P.C., 10th floor, 1177 West Loop South, Houston,  
TX 77027-9095 (US).

(81) Designated States: AU, CA, JP, European patent (AT, BE,  
CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT,  
SE).

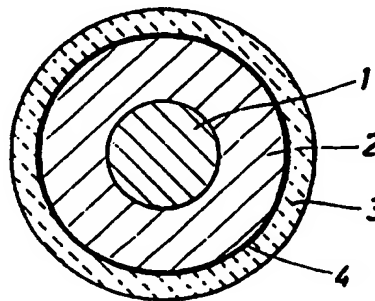
**Published**

*With international search report.  
Before the expiration of the time limit for amending the  
claims and to be republished in the event of the receipt of  
amendments.*

(54) Title: WEAR RESISTANT TRIBOSYSTEM

(57) Abstract

Surface and near surface hardened wear resistant tribological system articles of manufacture are provided. These tribological system articles are fabricated from titanium alloys that contain an amount of zirconium sufficient to permit the formation of a significant amount of zirconium oxide at the surface of the article to cause surface hardening and improved wear and abrasion resistance. Further, the zirconium-containing titanium alloy tribological articles are characterized in having an alloy substrate with an oxygen-rich layer surrounding the substrate, and a surface layer, overlying the oxygen-rich layer, including mixed oxides of the metals present in the alloy. A zirconium-rich interface may sometimes be present between the oxygen-rich layer and the mixed-oxide surface layer. The method of producing these surface hardened articles includes the steps of heating the article in an oxygen containing environment at a temperature sufficient to allow oxygen to diffuse to and react with the surface and near surface.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

### WEAR RESISTANT TRIBOSYSTEM

This invention relates to surface hardened zirconium-containing titanium wear resistant tribosystems, which are composed of articles of manufacture that are subject to wear, and in particular such hardened tribosystems where at least a portion of the surface and near surface region of system components is comprised of a mixed-oxide surface layer and an underlying near-surface-oxygen-rich solution layer. A zirconium-rich interface is present, in some instances, between the mixed oxide layer and the oxygen-rich solution. In particular, these surface hardened zirconium-containing titanium tribosystems may be produced by an elevated temperature process which permits the diffusion of oxygen into the near surface of the tribosystems. This invention is useful in applications which require the use of a wear resistant tribosystems such as aerospace, automotive, oil well, chemical pumping, fasteners, sporting equipment and marine applications.

Tribology is the science of wear. A tribological system is a system in which one or more components, which are articles of manufacture, of the system are subjected to wear, i.e. the gradual removal of material from a solid surface due to a rolling or sliding motion relative to another solid surface or due to impact or impingement by hard counter-surfaces or fluid particles.

25

Titanium alloys are used extensively in many tribological system applications such as aerospace, automotive, marine, pumps, fasteners, and piping systems due to their high strength, low density, corrosion resistance, and high temperature tolerance. However, a major disadvantage of titanium alloys is their sub-optimal tribological behavior, i.e. their susceptibility to wear. Wear of titanium alloys occurs

by several mechanisms such as: (i) abrasive (cutting) wear, (ii) adhesive (galling or scuffing) wear, (iii) oxidative (corrosive) wear, and (iv) erosive or fretting-type wear.

- 5 Titanium alloys, being relatively soft, are susceptible to abrasion or scratching by harder counter-bearing surfaces or other hard debris which may be present in between the bearing surfaces. Titanium alloys are also susceptible to adhesive wear, often called "galling," essentially sticking together of mating titanium parts which move against each other. This is a significant problem in many applications such as valves, rivets, fasteners, etc.

- When titanium or its alloys are exposed to oxygen, e.g. in air, they spontaneously form a thin passive oxide film even at room temperature.
- 15 However, this oxide is not very adherent and is easily removed due to abrasion by a counter-bearing surface, thus exposing fresh metal for additional passive oxide formation. This cyclic process is called oxidative wear and it is accelerated in the presence of a corrosive environment or third body particles (debris). The relative softness of these alloys also makes them susceptible to erosive wear, i.e. material removal due to impingement of solid particles or drops of liquid or gas. This is especially important in thin sections such as moving blades, valve constructions, pipe joints and bends, engine vanes, oil industry applications, etc.

25

- Fretting wear is observed when components are subjected to small vibratory movements relative to each other. This affect is initiated by adhesion, amplified by corrosion and has its main effect by abrasion. Fretting wear frequently occurs between components which are not intended to move relative to each other, e.g. press fits, shrink fits, bolted parts and splines. Fretting wear is exacerbated in the presence of a corrosive atmosphere.
- 30

The key to reducing the severity of most of these forms of wear is to increase the surface hardness of the titanium alloy. Numerous methods have been proposed for increasing the surface hardness and reducing the wear and galling of titanium alloys. Ceramic coatings, such as titanium nitride, have been deposited on these alloys by processes such as physical vapor deposition and chemical vapor deposition (see, for example, U.S. patent 4,687,487 to Hintermann). However, these ceramic coatings are much harder and stiffer than the base alloy substrate so that there is an abrupt mismatch in the stiffness of the coating and the substrate at the interface between the two. The elastic modulus (stiffness) of a titanium nitride coating is typically about 400 GPa while that of most titanium alloys is about 65 to 130 GPa. This modulus mismatch leads to undesirable stresses at the interface, especially when these components are bent or deformed in any manner, and increases the potential for the coating separating from the substrate by a delamination or spalling mechanism. Further, these types of "overlay coatings" are extremely sensitive to surface cleanliness and how the surface coating is formed. Often, the nucleation and growth of these types of coatings results in oriented, columnar grain structure within the coating, which may weaken the strength and abrasion (wear) resistance of the coating.

Attempts have been made to harden titanium alloys by nitrogen or oxygen ion implantation. In these processes, the titanium alloy substrate is bombarded with nitrogen or oxygen ions using a high voltage apparatus which forces the ions to penetrate the substrate. However, these processes affect the surface to a depth of only about 0.1 micron and peak hardness is not at the surface but slightly below the surface. Hence, the hardened surface tends to wear through relatively quickly.

Titanium alloys have also been hardened by processes such as gas nitriding and salt bath nitriding. These processes also produce a titanium nitride surface on these alloys by penetration of nitrogen into the metal substrate. However, as mentioned above, titanium nitride has a much higher stiffness than the titanium alloy base material, thus being potentially susceptible to detachment from the substrate by delamination or spalling.

10        There have been a few attempts at oxygen diffusion hardening of titanium alloys, such as for instance disclosed by Streicher, et al., in two conferences (CIMTEC, 1990, Italy, and European Society of Biomechanics, July 8-11, Denmark). However, the alloy used by Streicher, et al., is Ti-6Al-7Nb, which when oxidized would be expected to produce titanium oxide (TiO) or titanium dioxide (TiO<sub>2</sub>), both of which have very low shear strength and would be susceptible to detachment.

British Patent No. 1351062 discloses a process for surface hardening a titanium article by heating it in an atmosphere of air, nitrogen, hydrogen or oxygen. However, if heated in air, the surface would be expected to consist of titanium oxide (TiO), titanium dioxide (TiO<sub>2</sub>), or titanium nitride with the associated disadvantages described above. If heated in nitrogen, the surface produced would consist of titanium nitride with the associated stiffness mismatch disadvantage described above. If heated in hydrogen, the compound produced would be titanium hydride which is known to severely embrittle and be detrimental to the fatigue strength of titanium alloys. If heated in oxygen, the surface would be expected to consist of titanium oxide (TiO) or titanium dioxide (TiO<sub>2</sub>) with the associated low shear strength described above.

U.S. patent 5,372,660 to Davidson et al. discusses surface hardened zirconium-containing titanium alloy implants and is hereby fully incorporated by reference as if fully set forth. The major emphasis in 5,372,660 is the benefits that accrue from the use of surface hardened systems in the specialized area of medical implants and how such implants may be produced.

Clearly, the development of an effective means for increasing the surface hardness and wear resistance of titanium alloy articles of manufacture would be extremely beneficial for all tribological systems in which such articles are used. A titanium alloy surface which is highly wear resistant will produce less wear debris which will increase the expected service life of the article and require less frequent replacement.

The invention provides novel surface and near-surface hardened zirconium containing titanium alloy articles of manufacture for use in tribological systems for enhanced wear resistance. While the titanium alloys may optionally contain other alloying elements, the presence of zirconium is essential. Thus, the alloys are herein referred to as "titanium-zirconium" (Ti-Zr) alloys even though the zirconium content may be quite low and other alloying metals may be present in larger quantity.

25

The hardened Ti-Zr tribological systems described herein include articles which have a complex oxide film containing mixed titanium and zirconium oxides at the article's surface. Immediately underlying this mixed-oxide film is a region of oxygen-rich metal alloy. Underlying the oxygen-rich alloy layer is the substrate zirconium-containing titanium alloy. The interface between the oxygen rich alloy and the oxide regions may, in some instances, be zirconium-rich in comparison to the

underlying zirconium-containing titanium alloy. This method of producing a hard surface layer also produces a surface layer that is essentially constantly nucleating new surface oxide and thus grain size and other features of the microstructure within the hard oxide surface layer is extremely refined in comparison to "overlay" coating processes described earlier.

An illustrative diagram, not to scale, of a cross section of an article of an invention surface hardened tribological system is shown in the schematic diagram of Figure 1. The substrate zirconium-containing titanium alloy 1 is covered by a layer of oxygen-rich alloy 2 which in turn is covered by the surface layer of mixed-oxides 3. The thin interface 4 shown between the oxygen-rich alloy is not always obtained and is zirconium-rich.

15

This invention is particularly useful if the hardened substrate alloy is the Ti-Nb-Zr alloy, described in our co-pending application, U.S. serial number 08/036,414, filed March 24, 1993, which is a related application of U.S. patent 5,169,597, both of which are hereby incorporated by reference as if fully set forth.

20

One embodiment of the surface and near surface hardened Ti-Zr tribosystem articles described herein is comprised of an alloy that includes niobium, a Ti-Nb-Zr alloy, that has a complex oxide surface film, consisting of any or all of  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{TiO}$ ,  $\text{ZrO}_2$ ,  $\text{ZrO}$ ,  $\text{NbO}$  and  $\text{Nb}_2\text{O}_5$  and several suboxides, at the alloy surface. Underlying this mixed oxide film is a region of oxygen-rich alloy. The interface between the oxygen rich alloy and the mixed oxide regions may be zirconium-rich in comparison to the underlying zirconium-containing titanium alloy.

25  
30

The surface and near surface hardened zirconium- containing titanium tribological systems described in the current application may



be produced by an elevated temperature Oxygen Diffusion Hardening process which significantly hardens the surface and "near surface" of the alloy.

5        The presence of zirconium in the titanium alloy is required to ensure formation of a mixed oxide surface film containing zirconium dioxide (Zirconia,  $ZrO_2$ ), a ceramic with outstanding attachment to the base alloy and excellent wear resistance. Formation of this ceramic surface by oxidation of zirconium alloys using other processes than  
10    herein disclosed, is described in U.S. Patents 5,152,794 and 5,037,438, which are hereby incorporated by reference as if fully set forth. The inventions described in the present application are tribological systems of titanium-zirconium alloy with a wear-resistant hardened surface region formed by an oxygen diffusion process.

15        The mixed-oxide surface film permits the mass transport of oxygen, even at moderate temperatures, into the "near surface" of the metal alloy, underneath the mixed-oxide film. The diffusion of oxygen through the mixed-oxide film into the metal alloy creates a solid solution  
20    of the alloy and oxygen, which greatly increases near surface hardness. The deeper this solid solution extends, the thicker the hard surface. However, to obtain thicker solution layers, the tribological system must be subjected to heat treatment for longer periods of time and this longer heat treatment reduces fatigue strength. Consequently,  
25    to maintain fatigue strength, it is preferred that the tribological system only be heated to produce an oxygen solid solution layer that is less than about 50 microns thick, and more preferably less than about 20 microns thick.

30        The diffusion hardening process of the invention can be performed over a broad range of temperatures, but preferably between 200°C and 1200°C. The amount of time required at a given

temperature to effectively produce the surface and near surface hardened Ti-Zr alloy is related exponentially, by an Arrhenius-type relationship, to the temperature, i.e., shorter periods of time are required at higher temperatures for effective diffusion hardening.

5

The process of the invention requires a supply of oxygen to the Ti-Zr alloys which are being processed, along with exposure to elevated temperatures. The oxygen required for the diffusion hardening process may be supplied by a pure oxygen or oxygen-  
10 containing atmosphere, i.e., one that contains oxygen or compounds which are partially composed of oxygen such as H<sub>2</sub>O (water or water vapor), CO<sub>2</sub> (carbon dioxide), NO<sub>2</sub> (Nitrogen dioxide), SO<sub>2</sub> (sulfur dioxide), or any other gaseous, liquid or solid compounds capable of disassociation to produce oxygen at elevated temperatures and/or  
15 reduced pressures. Inert gases such as argon, helium or nitrogen may be used as a carrier medium for the oxygen-containing compound.

Figure 1 is an illustrative cross-sectional schematic diagram of a surface and near surface hardened titanium alloy containing zirconium.

20

Figure 2A is a bar graph comparing the Knoop hardness values (10 grams) for the surfaces of the invention, produced by aging the Ti-Nb-Zr alloys for 6 hours at 500°C in an air atmosphere, with other materials which have been aged in the same manner. The alloys and  
25 materials are:

A = Ti-16Nb-17Zr	F = Ti-12Nb-13Zr
B = Ti-16Nb-13Zr	G = Ti-9Nb-8Zr
C = Ti-13Nb-8Zr	H = Ti-17Nb
30 D = Ti-12Nb-17Zr	I = Ti-12Nb
E = Ti-10Nb-13Zr	J = Ti-9Nb

Figure 2B is a bar graph comparing the Knoop hardness values (25 grams) for the surfaces of the invention, produced by aging Ti-Nb-Zr alloys for 6 hours at 500°C in an air atmosphere, with other materials which have been aged in the same manner. The key to identify alloys and materials is as for Figure 2A.

Figure 2C is a bar graph comparing the Knoop hardness values (100 grams) for the surfaces of the invention, produced by aging Ti-Nb-Zr alloys for 6 hours at 500°C in an air atmosphere, with other materials which have been aged in the same manner. The key to identify alloys and materials is as for Figure 2A.

Figure 3A is a bar graph comparing the Knoop hardness values as a function of load (5-100 grams) of several alloys of the invention with other materials. In Figures 3A-B, the alloys of the invention and the other materials are identified as follows:

K = non-hardened Ti-13Nb-13Zr  
L = hardened Ti-13Nb-13Zr  
M = hardened Ti-6Al-4V  
N = hardened Ti-16Nb-17Zr  
O = hardened Ti-16Nb-13Zr

Figure 3B is a bar graph comparing the Knoop hardness values as a function of load (5-500 grams) of several alloys of the invention with other materials. The key to identify the alloys and other materials is as for Figure 3A.

Figure 4A is a bar graph comparing the ratio for the (011) reflection for the expanded Alpha HCP structure in the near surface to the Alpha HCP structure of the bulk alloy, for several surface hardened alloys of the invention produced by aging the substrate alloys for 6

hours at 500°C in an air atmosphere. The alloys are identifiable by the same key for alloys A-G given in the description of Figure 2A.

Figure 4B is a bar graph comparing a qualitative ranking of the lattice distortion observed for the (002) and (001) reflections for several alloys of the invention produced by aging the substrate alloys for 6 hours at 500°C in an air atmosphere. The alloys are identifiable by the same key for alloys A-G given in the description of Figure 2A.

Figure 5 is an oxygen concentration versus depth curve for the invention produced by subjecting Ti-13Nb-13Zr alloy to a diffusion hardening process including heating up from room temperature to 500°C in 2.5 hours, a 6 hour soak at 500°C, and cooling to room temperature in 10 hours.

15

Figure 6 shows the near surface hardness (measured by Nano Indentor) for the surface and near surface hardened Ti-13Nb-13Zr alloys of the invention and several other processed materials. The alloys and materials may be identified as follows:

20

P = titanium nitride

Q = oxygen surface hardened Ti-13Nb-13Zr

R = ion-implanted Ti-6Al-4V

S = zirconium oxide

25

Figure 7 shows the modulus of elasticity (stiffness) as a function of depth for the surface and near surface hardened Ti-13Nb-13Zr alloys of the invention and several other processed materials. The alloys and materials are identifiable by the same key for alloys P-S given in the description of Figure 6.

30

While not wishing to be bound by any theory, the inventors offer the following explanation of the invention. The inventors believe that the oxidation of metals and metal alloys (such as the oxygen diffusion hardening process preferred to produce the invention) occurs by one of  
5 two primary mechanisms: p-type and n-type oxidations. N-type occurs by the diffusion of oxygen anions into the metal and p-type occurs by the diffusion of metal cations outwards towards the surface (oxygen bearing environment). Iron and copper are classic examples of p-type oxidation while titanium, zirconium and aluminum are examples of n-  
10 type oxidation. The oxidation of all metals is facilitated by the presence of crystal lattice defects which promote the movement of both anions and cations through the metallic and oxide crystal lattices.

The oxygen diffusion hardening process preferred for production  
15 of the invention tribological system articles occurs by diffusion of oxygen into the preferred zirconium-containing titanium alloy to significant depths below the surface (1-50 microns depending on the time, temperature and Zr content). Titanium alloys which do not contain zirconium will be penetrated by oxygen to much smaller depths  
20 at comparable temperatures for comparable heating times. These titanium oxide layers are not tightly adherent and therefore not useful in tribological systems.

The presence of zirconium in titanium greatly increases the rate  
25 of diffusion of oxygen through the surface mixed oxide into the underlying substrate, by orders of magnitude. This occurs due to the increased number of defects within the oxide lattice caused by the presence of zirconium which permits the exchange of oxygen from the oxygen-rich environment into the oxygen-deficient metal alloy. In  
30 addition, zirconium is a highly oxygen-active element and, as such, may tend to segregate to the very surface of a polished, unoxidized surface and at the oxide-metal interface.

The invention provides useful tribological system articles of all kinds, including but not limited to tribological system applications in aerospace, automotive, marine, sporting goods, pumps, piping  
5 systems, bicycle chains, gears and other components, gun barrels, springs, rivets, fasteners, connecting rods, crank shafts, oil platform components, oil patch seals and pumps, moving blades, valve constructions, deep submersibles, pipe joints and bends, engine vanes, press fits, shrink fits, bolted parts and splines. Any application in which  
10 one or more articles of manufacture are subject to wear is a good candidate for utilization of the surface and near surface hardened zirconium-containing titanium tribological system articles described above.

15 The preferred diffusion hardening process can be performed by subjecting components of the tribosystem to a sufficiently high temperature in the presence of oxygen for a time sufficient to form the hardened surface. Temperatures may preferably range from between about 200°C and about 1200°C more preferably between about 200  
20 and 700°C, most preferably about 500°C. The amount of time required at a given temperature to effectively harden a Ti-Zr alloy depends upon the temperature used, i.e., shorter periods of time are required at higher temperatures.

25 The oxygen required may be supplied by an environment containing oxygen or an environment able to provide oxygen under the thermal conditions of oxidation. Thus, the environments include pure oxygen or an oxygen-containing atmosphere, i.e., containing oxygen or compounds which are partially composed of oxygen such as H<sub>2</sub>O  
30 (water or water vapor), CO<sub>2</sub> (carbon dioxide), NO<sub>2</sub> (nitrogen dioxide), SO<sub>2</sub> (sulfur dioxide), or any other gaseous, liquid or solid compounds capable of dissociation to produce oxygen at elevated temperatures.

Inert gases such as argon, helium or nitrogen may be used as a carrier medium for oxygen or oxygen-bearing compounds.

In the most preferred embodiment, the furnace may be purged  
5 with argon to remove oxygen. This elimination of oxygen minimizes the amount of molecular oxygen present and allows the formation of thicker coatings with atomic oxygen formed from the disassociation of an oxygen-containing compound, such as water vapor, and the like. But if thinner hardened layers are desired, then some molecular oxygen is  
10 desirably present in the furnace. In the preferred method of the invention, the surface layers of the hardened titanium alloy are produced by a diffusion hardening process using argon as the carrier gas. This carrier gas is most preferably bubbled through a water bath in order to saturate it with water prior to continuous introduction into the  
15 diffusion hardening furnace containing the Ti-Zr alloy tribosystem component to be surface hardened. As the temperature of the water vapor increases in the furnace, the water vapor dissociates at the tribosystem component surface to produce atomic oxygen which diffuses into the titanium-zirconium tribosystem component surface  
20 being treated, to produce a hardened surface. The extent of dissociation of water vapor increases with increasing temperature.

The hardened surface preferably has a mixed oxide layer in the range from about 0.1 to about 10 microns thick. Preferably, the  
25 oxygen-rich layer is from about 1 to about 50 microns thick.

This diffusion process employed to produce the invention may be carried out at atmospheric pressure. It may also be carried out at a reduced pressure to facilitate generation of oxygen from oxygen-  
30 containing compounds such as H<sub>2</sub>O (water or water vapor), CO<sub>2</sub> (carbon dioxide), NO<sub>2</sub> (nitrogen dioxide), SO<sub>2</sub> (sulfur dioxide) etc. Diffusion into the tribosystem may also be facilitated by use of high

pressures, in combination with elevated temperatures. The most preferred range of pressures for this process is from about  $10^{-6}$  torr to about  $7.6 \times 10^6$  torr.

5           A particularly preferred embodiment of the invention is a tribosystem made of surface hardened Ti-Nb-Zr alloys. The most preferred embodiment is a tribosystem comprised of surface hardened Ti-13Nb-13Zr alloy as described in our U.S. patent 5,169,597 incorporated by reference.

10

The most preferred temperature cycle used for producing the diffusion hardened tribosystems of Ti-13Nb-13Zr includes subjecting the tribosystem to an oxygen environment preferably created by an inert gas carrying water vapor (as described above); heating from room  
15   temperature to about 500°C in about 2.5 hours; soaking for about 6 hours at about 500°C; then cooling to room temperature in 1-10 hours; and removing from the oxygen environment.

The following examples serve solely as illustrations of the  
20   invention as described above and claimed below and are not intended to limit the scope of the invention in any way.

#### Example 1

A series of surface and near surface hardened Ti-Nb-Zr alloys  
25   were produced through diffusion hardening in an air atmosphere. The thermal cycle consisted of a ramp up from room temperature to 500°C in 2.5 hours, a 6 hour soak at 500°C and air cooling to room temperature. Figures 2A, 2B and 2C contain Knoop micro-hardness values showing that near surface hardness increases with zirconium  
30   content of the alloy. The titanium alloys which did not contain zirconium were not diffusion hardened. Figures 3A and 3B are plots of Knoop hardness values for Ti-13Nb-13Zr, Ti-16Nb-17Zr, Ti-16Nb-13Zr



and Ti-6Al-4V after the diffusion hardening process and of Ti-13Nb-13Zr without diffusion hardening. These two plots show that surface hardness of Ti-6Al-4V (the most commonly used titanium alloy in

5 aerospace and most other applications) was not affected by the diffusion hardening process at this temperature. This is due to the absence of zirconium. The titanium alloys according to the invention, which contain zirconium, showed improved surface hardness after being subjected to the diffusion hardening process.

10

### Example 2

Surface hardened Ti-13Nb-13Zr discs were produced in an atmosphere containing argon, oxygen and water vapor. The diffusion hardening process was performed in an argon/oxygen/water vapor

15 mixed atmosphere during a cycle including increasing temperature from room temperature to 500°C in 2.5 hours, soaking at 500°C for 6 hours, and cooling to room temperature in 10 hours. These specimens were subjected to sliding wear against hemispherical pins of polymethylmethacrylate (PMMA) which contained particles of zirconia.

20

The results, given in Table 1, show that invention surface and near surface hardened Ti-13Nb-13Zr disc are several orders of magnitude more wear resistant than Ti-6Al-4V or Ti-13Nb-13Zr.

Table 1

Material	Wear Track Depth ( $\mu\text{m}$ )
Ti-6Al-4V	$21 \pm 9$
Nitrogen ion implanted Ti-6Al-4V	$17 \pm 10$
Non-diffusion-hardened Ti-13Nb-13Zr	$21 \pm 3$
Diffusion hardened Ti-13Nb-13Zr	$0.15 \pm 0.01$
ASTM F-799 Co-Cr-Mo	$0.8 \pm 0.2$

Example 3

Surface and near surface hardened Ti-Nb-Zr alloys were

- 5 produced by subjecting the substrate alloys to a diffusion hardening process in an air atmosphere. The diffusion hardening process was performed in air under a heating cycle including increasing temperature from room temperature to 500°C in 2.5 hours, soaking at 500°C for 6 hours, and air cooling to room temperature. These specimens were
- 10 analyzed by x-ray diffraction. Figures 4A and 4B are bar graphs resulting from analysis of x-ray diffraction data. Figure 4A ranks the amount of near surface crystal lattice distortion for seven Ti-Zr-Nb alloys. The increase in surface hardness is caused by lattice distortion due to the presence of oxygen in solid solution in the near surface.
- 15 Lattice distortion is a measure of the effectiveness (the amount of oxygen in solid solution) of the diffusion hardening process. Figure 4B ranks the same seven alloys based on a qualitative comparison of the x-ray diffraction profiles. Inspection of Figures 4A and 4B show them to be in excellent agreement—the hardening effect increases with
- 20 zirconium content of the alloy.

Example 4

Surface and near surface hardened Ti-13Nb-13Zr alloy discs were produced by subjecting the substrate alloy to diffusion hardening in an atmosphere consisting of argon, oxygen and water vapor. The diffusion hardening process was performed during a thermal cycle including heating from room temperature to 500°C in 2.5 hours, soaking at 500°C for 6 hours, and cooling to room temperature in 10 hours. These specimens were analyzed using secondary ion mass spectrometry (SIMS). Figure 5 is the oxygen profile obtained by SIMS, showing significant oxygen penetration of a depth of 2-3 microns below the surface.

Example 5

Surface and near surface hardened Ti-13Nb-13Zr discs were prepared in an atmosphere consisting of argon, oxygen and water vapor. The diffusion hardening process was performed during a cycle including heating from room temperature to 500°C in 2.5 hours, soaking at 500°C for 6 hours, and cooling to room temperature in 10 hours. These specimens were analyzed using x-ray photoelectron spectrometry (XPS). Table 2 contains the surface chemistry data collected using XPS, showing that the surface oxide is a mixture of ZrO, ZrO<sub>2</sub>, TiO<sub>2</sub>, TiO, Ti<sub>2</sub>O<sub>3</sub>, NbO and Nb<sub>2</sub>O<sub>5</sub> and several suboxides. This mixed oxide structure provides for a dense, adherent oxide layer which enhances the abrasion resistance of the material. The XPS analyses also showed significant concentrations of oxygen in solid solution within the near surface of the Ti-13Nb-13Zr alloy.

Table 2

Depth	TiO <sub>2</sub> /TiO <sub>2-x</sub>	TiO	TiO <sub>1-x</sub>	Nb <sub>2</sub> O <sub>5</sub>	Nb O	Nb <sub>1-x</sub> /Nb	ZrO <sub>2</sub>	ZrO <sub>2-x</sub>	Zr
50	84%	0	0	2%	0	0	14%	0	0
500	39%	4%	23%	3%	4%	9%	15%	2%	0
1000	25%	22%	29%	2%	3%	9%	7%	2%	2%
2500	20%	25%	36%	2%	4%	9%	3%	3%	3%

Example 6

Surface and near surface hardened Ti-13Nb-13Zr discs were prepared by diffusion hardening in an atmosphere consisting of argon, oxygen and water vapor. The diffusion hardening process was performed during a thermal cycle including heating from room temperature to 500°C in 2.5 hours, soaking at 500°C for 6 hours, and cooling to room temperature in 10 hours. These specimens were analyzed using a Nano Indentor and compared with a titanium nitride coating. Figure 6 contains the surface hardness data obtained using the Nano Indentor for zirconium dioxide and titanium nitride coatings, surface and near surface hardened Ti-13Nb-13Zr (produced by the method described above) and nitrogen ion implanted Ti-6Al-4V. Figure 6 shows that the hardness of the near surface of diffusion hardened Ti-13Nb-13Zr is comparable to that of ceramic coatings such as titanium nitride and zirconium dioxide. This again demonstrates the exceptionally high hardness of the surface and near surface hardened Ti-13Nb-13Zr. High hardness values are also achievable in other titanium alloys which contain sufficient zirconium as shown in Figures 2A, 2B and 2C.

Figure 7 shows the elastic modulus (stiffness), also obtained by Nano Indentation, of the hardened surface alloys produced by the diffusion hardening process, in comparison to that of zirconium dioxide and titanium nitride coatings. As seen from the figure, the modulus of the titanium nitride coating is significantly higher than that of the other two surfaces, thus producing a greater stiffness mismatch with resultant undesirable stresses at the interface.

Although the invention has been described with reference to its preferred embodiments, those of ordinary skill in the art may, upon reading this disclosure, appreciate changes and modifications which may be made and which do not depart from the scope and spirit of the invention as described above and claimed below.

**CLAIMS**

1. An article of manufacture with a hardened surface for enhanced wear resistance, said article comprising:
  - 5 (a) a zirconium-containing titanium alloy substrate;
  - (b) a layer, at least partially surrounding the substrate, of oxygen-rich alloy solution; and
  - (c) a surface layer, at least partially overlying the oxygen-rich alloy layer, of mixed oxides of metals present in the alloy substrate.
- 10 2. The article of claim 1, wherein the layer of oxygen-rich alloy solution and surface layer of mixed oxides are formed by subjecting the zirconium-containing titanium alloy substrate to elevated temperatures in an environment able to provide oxygen and from  
15 which oxygen can diffuse into the surface of the alloy.
3. The article of claims 1 or 2, wherein said layer of oxygen-rich alloy is less than about 50 microns thick.
- 20 4. The article of claims 1 or 2, wherein said layer of oxygen-rich alloy is less than about 20 microns thick.
5. The article of claims 1 or 2, wherein said surface layer of mixed-oxides is from about 0.1 to about 10 microns thick.
- 25 6. The article of claim 1 or 2, further comprising a zirconium-rich interface between the oxygen-rich layer and the mixed-oxide surface layer.
- 30 7. The article of claim 2, wherein the layers are formed at temperatures between about 200°C and about 1200°C.

8. The article of claim 1 or 2, wherein the layers are formed in an environment comprising oxygen-containing compounds which are partially composed of oxygen and that disassociate to produce oxygen at temperatures at which the layers form.
- 5
9. The article of claim 8, wherein inert gases are used as a carrier medium for the oxygen-containing compounds.
10. The article of claim 2, wherein the zirconium containing titanium alloy comprises:
- 10 titanium alloy comprises:  
titanium; from about 10 wt.% to about 20 wt.% niobium; and from about 0.5 wt.% to about 20 wt.% zirconium.
11. The article of claim 2, wherein the substrate metallic alloy comprises:
- 15 comprises:  
titanium; from about 35 wt.% to about 50 wt.% niobium; and from about 0.5 wt.% to about 20 wt.% zirconium.
12. The article of claim 2, wherein the substrate metallic alloy comprises:
- 20 comprises:  
about 74 wt.% titanium; about 13 wt.% niobium; and about 13 wt.% zirconium.
13. The article of claim 2, wherein the layers are formed by a process comprising the steps of:
- 25 process comprising the steps of:  
(a) exposing, at least a portion of the article to an oxygen-containing environment;  
(b) heating the article up to a temperature that allows oxygen to diffuse into at least a portion of surfaces of said article;
- 30 (c) soaking the article at the temperature for a time sufficient to oxidize elemental metal at the surface and near surface of the article;

(d) cooling the article to room temperature.

14. A process for manufacturing an article with a hardened surface for enhanced wear resistance comprising;

5 (a) exposing, at least a portion of the article to an oxygen-containing environment;

(b) heating the article up to a temperature that allows oxygen to diffuse into at least a portion of surfaces of said article;

(c) soaking the article at the temperature for a time sufficient  
10 to oxidize elemental metal at the surface and near surface of the article;

(d) cooling the article to room temperature.

15 15. The article of claim 13, wherein the heating is up to about 500°C in about 1 to about 10 hours;

the soaking is for about 2 to about 8 hours at about 500°C; and  
the cooling to room temperature is in about 1 to about 10 hours.

20 16. The article of claim 13 or 15, wherein the heating is in a furnace continuously supplied with oxygen-containing gasses.

25 17. An article of manufacture of a zirconium-containing titanium alloy with a hardened surface for enhanced wear resistance, the article produced by a process comprising the steps of:

(a) subjecting a zirconium-containing titanium article  
substrate to an environment able to provide oxygen;

(b) heating the zirconium-containing article substrate to a  
temperature that allows oxygen to diffuse into at least a portion of  
30 surfaces of said substrate;



(c) soaking the zirconium-containing article substrate at the temperature for a time sufficient to oxidize elemental metal at the surfaces of the substrate; and

- 5 (d) producing a hardened article comprising a hard mixed-oxide surface layer on the zirconium-containing article substrate and an oxygen-rich layer beneath said mixed oxide surface layer.

18. A process for manufacturing an article with a hardened surface for enhanced wear resistance comprising;

- 10 (a) subjecting a zirconium-containing titanium article substrate to an environment able to provide oxygen;

(b) heating the zirconium-containing article substrate to a temperature that allows oxygen to diffuse into at least a portion of surfaces of said substrate;

- 15 (c) soaking the zirconium-containing article substrate at the temperature for a time sufficient to oxidize elemental metal at the surfaces of the substrate; and

- (d) producing a hardened article comprising a hard mixed-oxide surface layer on the zirconium-containing article substrate and  
20 an oxygen-rich layer beneath said mixed oxide surface layer.

19. The article of claim 17, wherein the heating is up to from about 200 to about 700°C.

- 25 20. The article of claim 17, wherein the environment comprises argon, oxygen, and water vapor.

21. The article of claim 17, wherein the environment comprises a composition having chemically bound oxygen that is released for  
30 forming an oxide with elemental metal at article substrate surfaces during the steps of heating and soaking.

22. The article of claim 17, wherein the zirconium-containing titanium alloy is selected from the group of alloys consisting of:

(i) titanium, about 10 to about 20 wt.% niobium, and about 0.5 to about 20 wt.% zirconium; and

5 (ii) titanium, about 35 to about 50 wt.% niobium, and about 0.5 to about 20 wt.% zirconium.

23. The article of claim 22, wherein the mixed oxide layer is from about 0.1 to about 10 microns thick.

10

24. The article of claim 22, wherein the oxygen-rich layer is from about 1 to about 50 microns thick.

25. An article of manufacture with a hardened surface for enhanced wear resistance, said article comprising a zirconium-containing titanium alloy substrate and a hard mixed oxide surface on said substrate, the article produced by a process comprising the steps of:

15 (a) subjecting an article substrate comprising a zirconium-containing titanium alloy to an environment able to provide oxygen for oxidizing elemental metal at surfaces of the substrate;

(b) heating the article substrate in the environment to a temperature from about 200 to about 1200°C;

20 (c) soaking the article substrate at a temperature that permits oxidizing of elemental metal at substrate surfaces and diffusion of oxygen beneath the substrate surfaces; and

(d) producing a hard mixed-oxide surface layer on the zirconium-containing article substrate and an oxygen-rich layer beneath said mixed oxide surface layer.

30

26. The article of claim 25, wherein the zirconium-containing titanium alloy is selected from the group consisting of:

25

(i) titanium, about 10 to about 20 wt.% niobium, and about 0.5 to about 20 wt.% zirconium; and

(ii) titanium, about 35 to about 50 wt.% niobium, and about 0.5 to about 20 wt.% zirconium.

5

27. The article of claims 25 or 26, wherein the article of manufacture is selected from the group consisting of seals, fasteners, pipe joints, valves, pump articles, piping articles, aerospace articles, marine articles, and automotive articles, oil well application articles, sporting good articles, and cutting tool articles.

28. A process for manufacturing an article with a hardened surface for enhanced wear resistance comprising;

(a) subjecting an article substrate comprising a zirconium-containing titanium alloy to an environment able to provide oxygen for oxidizing elemental metal at surfaces of the substrate;

(b) heating the article substrate in the environment to a temperature from about 200 to about 1200°C;

(c) soaking the article substrate at a temperature that permits oxidizing of elemental metal at substrate surfaces and diffusion of oxygen beneath the substrate surfaces; and

(d) producing a hard mixed-oxide surface layer on the zirconium-containing article substrate and an oxygen-rich layer beneath said mixed oxide surface layer.

1/5

FIG. 1

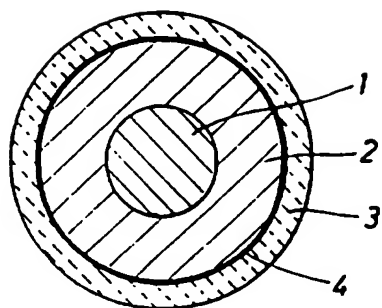


FIG. 2A

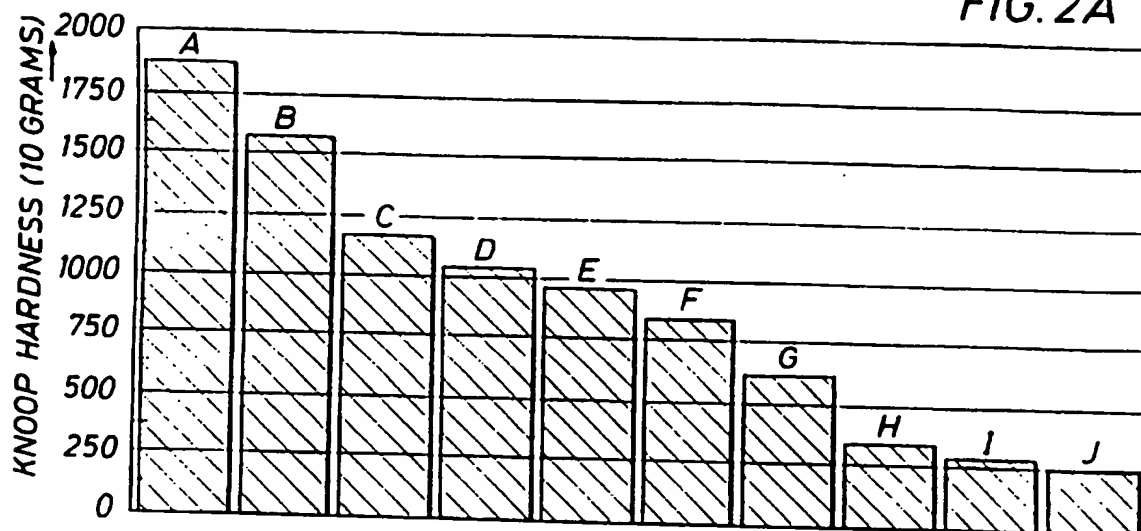
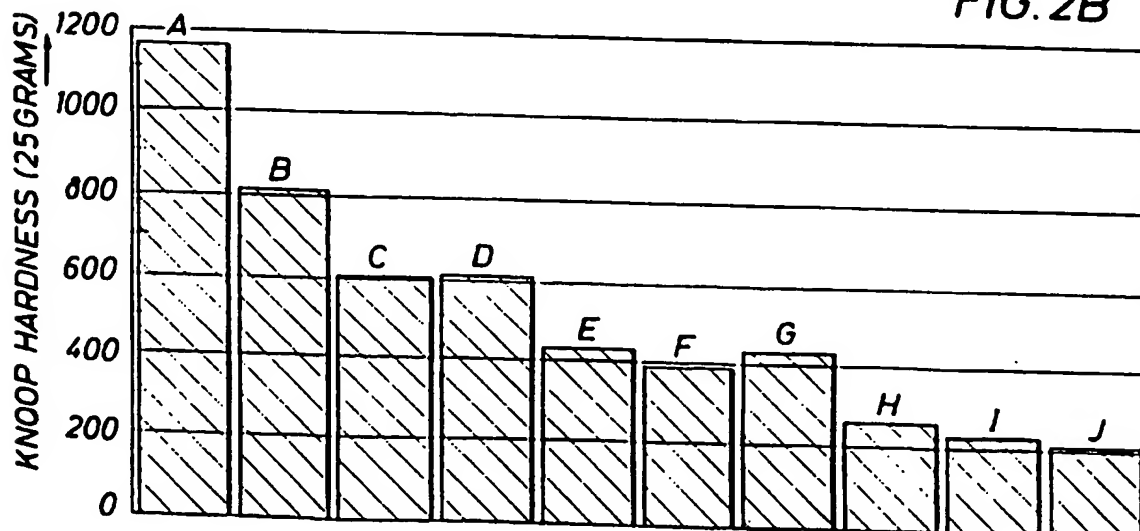


FIG. 2B



2/5

FIG. 2C

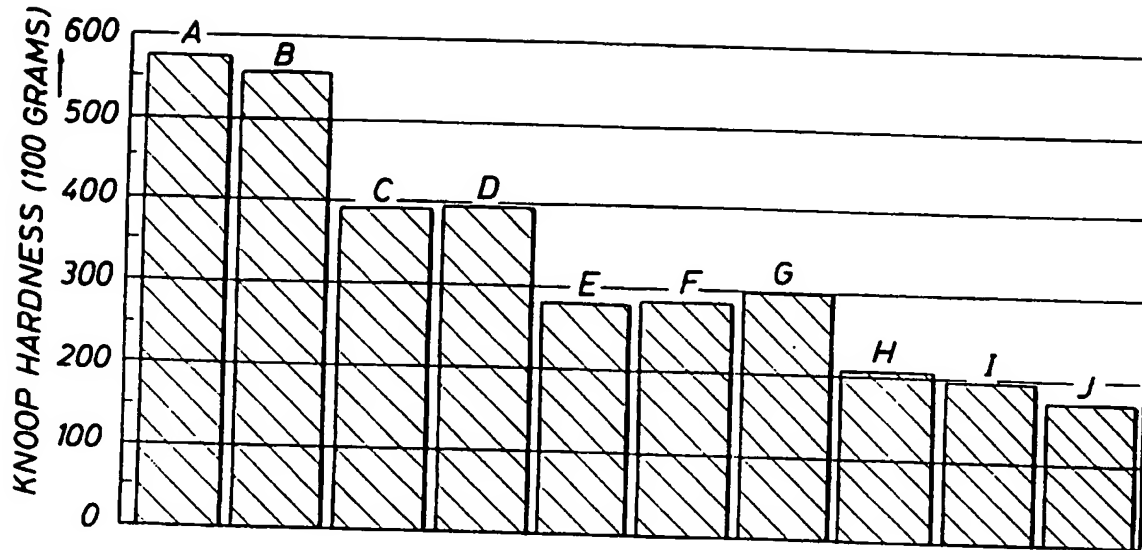
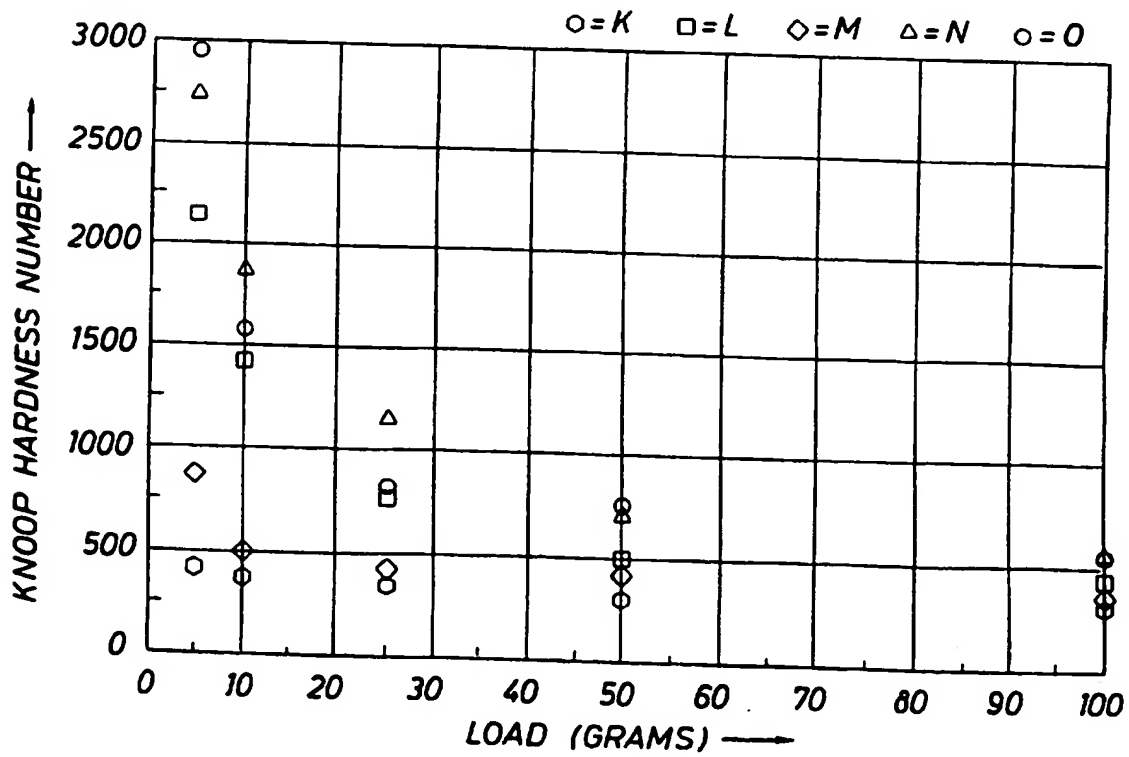


FIG. 3A



3/5

FIG. 3B

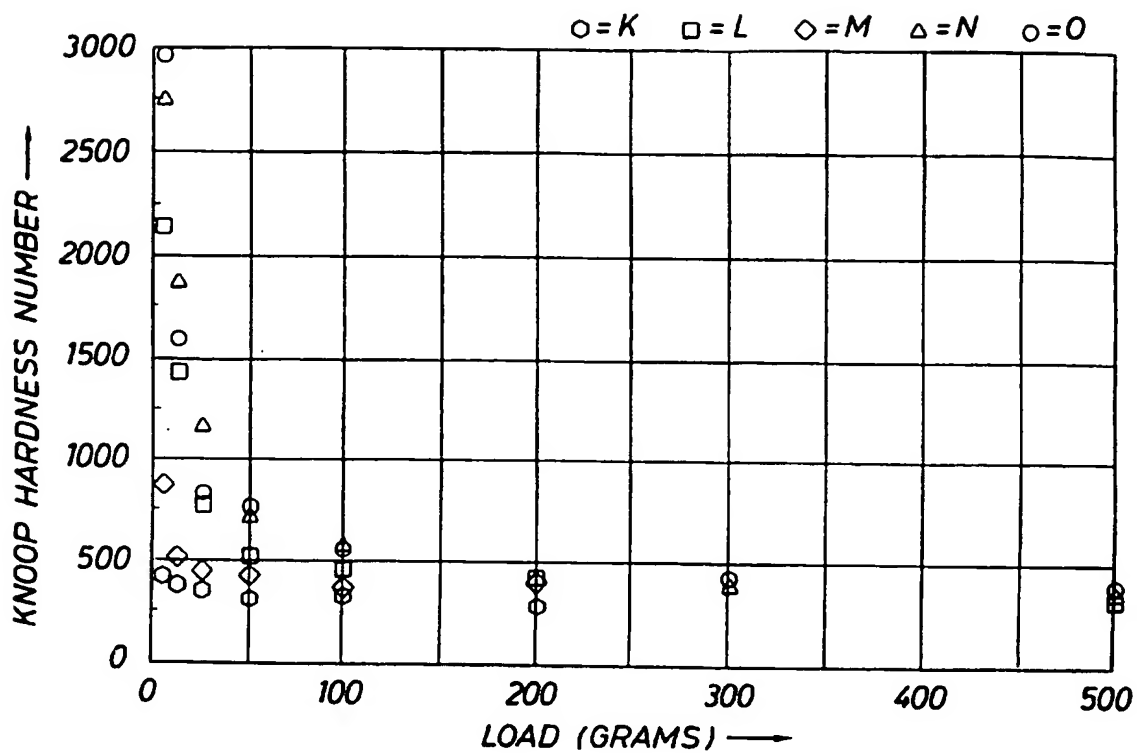
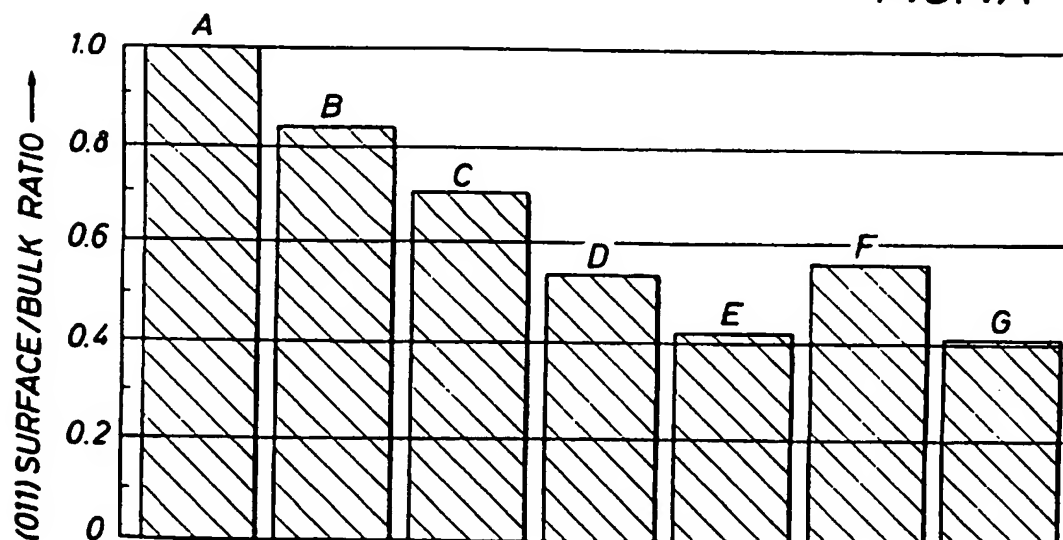


FIG. 4A



4/5

FIG. 4B

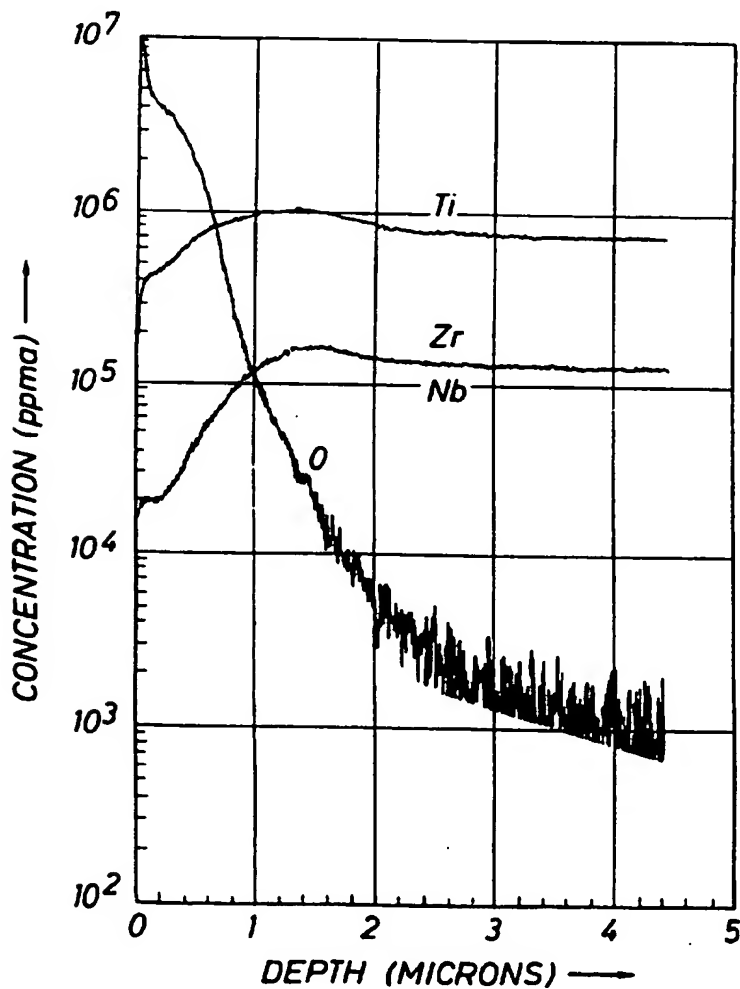
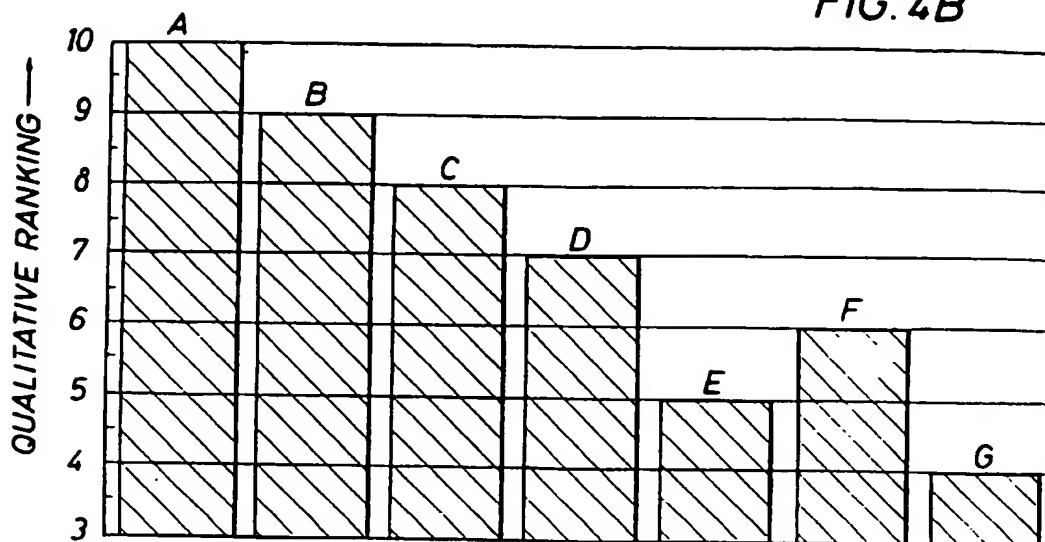


FIG. 5

5/5

FIG. 6

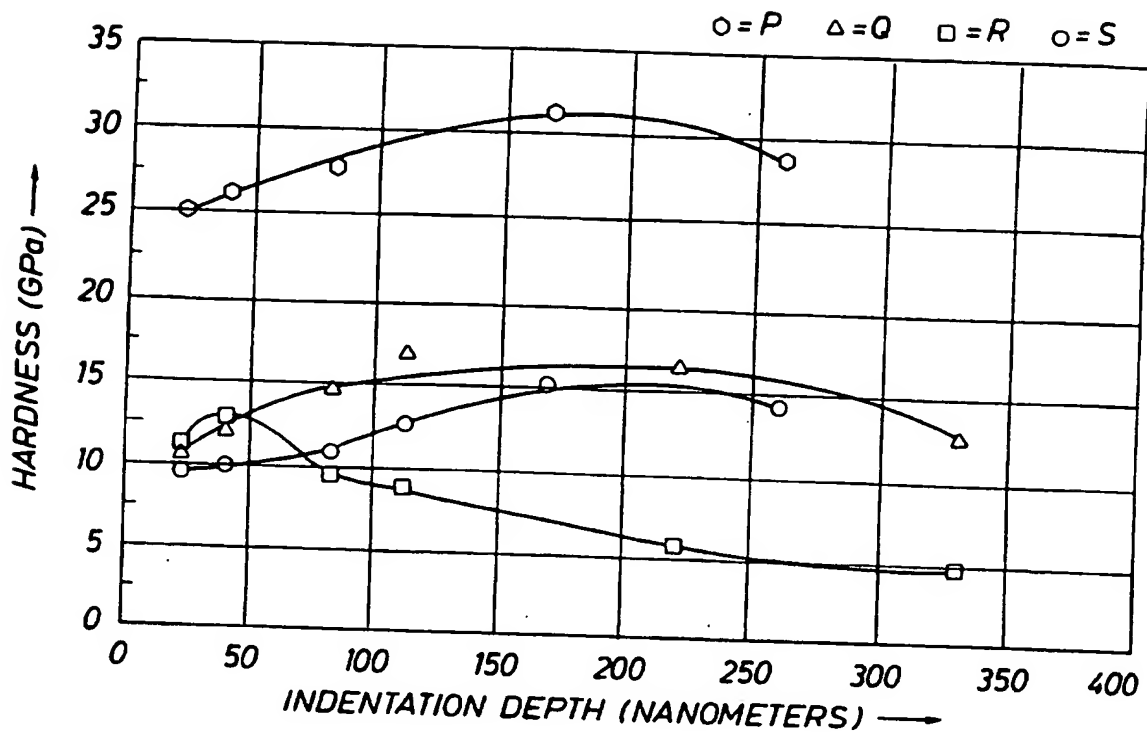
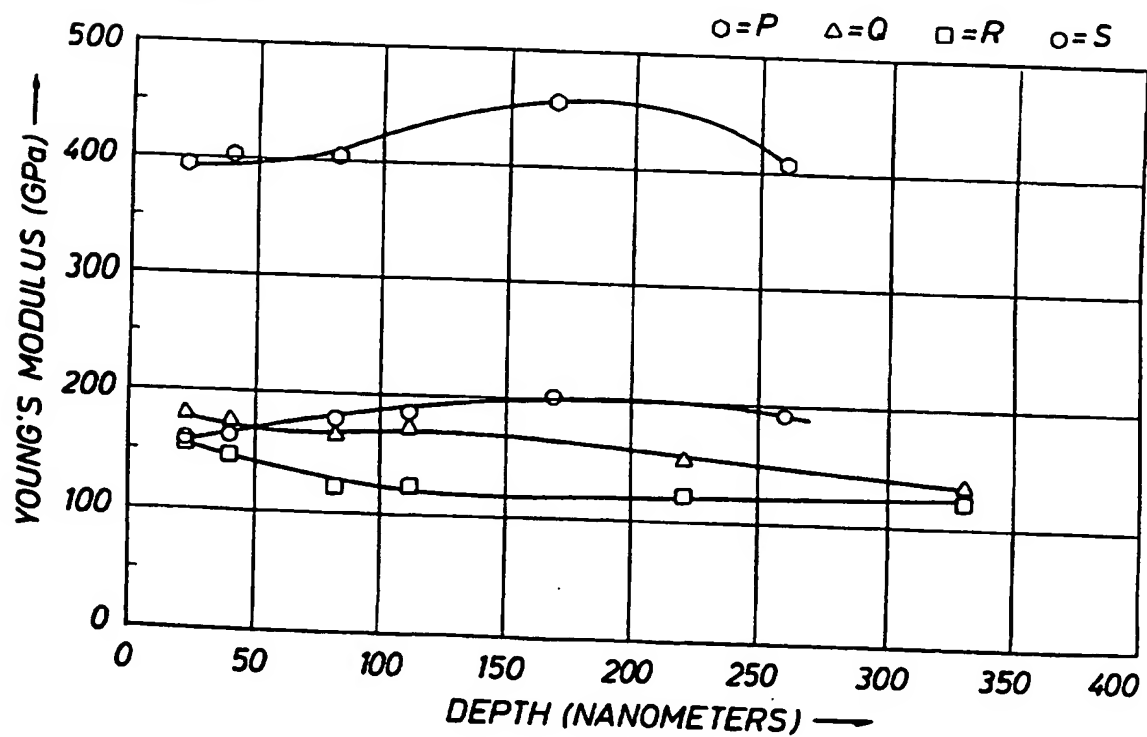


FIG. 7





## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US96/01123

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C22C 14/00; C23C 8/10

US CL : 148/421, 669

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/421,669

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,372,660 (DAVIDSON ET AL) 13 December 1994, col. 1, lines 18-62.	1-28
Y	US, A, 5,051,140 (MUSHIAKE ETAL) 24 September 1991, col. 6, lines 4-62.	1-28

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

* Special categories of cited documents:	
*A* document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*E* earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	*A* document member of the same patent family

Date of the actual completion of the international search

10 MAY 1996

Date of mailing of the international search report

30 MAY 1996

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SAM SILVERBERG

Telephone No. (703) 305-9646